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Heterogeneity of Metal Surfaces

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An atom is chemisorbed on a clean and bare metal surface by means of a number of covalent-resonating (metallic) bonds. If a fraction θ of this ideal surface is covered with adatoms, a double layer is set up which changes the work function of the adsorbent by an amount $\Delta\varphi$ and the adsorption heat by an amount Δq. If the adatoms do not interact, $\Delta\varphi$ and Δq vary linearly with θ. Moreover, $\Delta q = (n/2)\,\Delta\varphi$ where n is the number of valence electrons of the adatom taking part in the bonding. This effect is termed "induction." It provides a quantitative explanation of the fall in adsorption heat with coverage in all cases where pertinent data are available. Horizontal interactions between adatoms as well as heterogeneity existing prior to adsorption also contribute to the fall in adsorption heat on a real surface. Induction however is capable of explaining a number of facts which cannot be ascribed to the two other effects just mentioned. Some consequences of induction are pointed out in connection with problems in chemisorption and catalysis. In particular, the nature of "active centers" on a metal surface is elucidated.

A number of concepts have dominated the field of research in chemisorption and catalysis over a period of 25 years. Among these the idea of surface heterogeneity first clearly introduced by Taylor[1] with the hypothesis of active centers has been particularly fruitful. Of equal importance has been the recognition that the chemical interaction between molecules and surfaces is generally associated with an activation energy.[2] It seems appropriate to re-examine the concepts of active centers in the light of more recent work which has been concerned especially with the behavior of clean metal surfaces. It will be remarked at the start that our rapidly growing knowledge of chemisorption at clean surfaces will be the basis of the present discussion on surface heterogeneity and activated adsorption. As will be seen, there is no contradiction between the data obtained with clean surfaces on the one hand and with contaminated surfaces on the other hand: heterogeneity and activated adsorption on the latter find their ultimate explanation in the properties of the former.

Chemisorption of Non-metallic Atoms on a Metal Surface.—Let us consider first a clean metallic adsorbent bounded by a single crystallographic plane. Such an ideal surface may be termed *a priori* homogeneous: all adsorption sites are equivalent before chemisorption sets in. A non-metallic atom may now be chemisorbed on this bare surface: it will make chemical bonds with the surface atoms surrounding the adsorption site, the number of these bonds depending on the size of the adatom and the lattice spacing of the exposed plane. The heat q_0 corresponding to this surface solution can only be evaluated with the help of a correct model of the chemisorption bonds. Let us first examine the case of hydrogen. When hydrogen is dissolved in a metal, the field of the proton is screened to such an extent by the metallic conduction electrons that no bound state is possible. This collectivization of the valence electron of hydrogen by the metal has first been demonstrated by Mott[3] without taking into account the exchange forces and more recently, it has been shown to be generally valid by Isenberg[4] who used a semi-classical model with exchange forces. Thus the bonds between hydrogen and its metallic neighbors are essentially metallic in character or of the resonating covalent type of Pauling. These covalent bonds will have a certain degree of ionicity according to the relative electronegativities of hydrogen and the metal in question. This picture is in agreement with the magnetic properties of solutions of hydrogen in palladium,[5] with the electrolysis of the same solid solutions[6] and with the change in hydrogen solubility of various metals due to alloying elements.[7,8]

The same picture must remain essentially valid for the surface solution of hydrogen. Consequently, the valence electron of hydrogen is collectivized by the metallic electrons at the surface and resonating covalent bonds having some ionic character possesses a dipole moment and the resulting dipole moment along an axis perpendicular to the surface will be called the effective dipole moment M_0. It is to be noted that M_0 is *not* the dipole moment associated with each individual bond between hydrogen and a neighboring metal atom. In particular, it is conceivable that M_0 may be zero or very small even if the individual dipole moments are not. The sign of M_0 is no indication of the sign of the individual dipoles since the adsorbed atom may penetrate below the outermost layer of metal atoms so that for instance M_0 may be negative outward even if the positive end of the individual dipoles is at the adsorbed atom. This interstitial adsorption which represents the preliminary step toward bulk diffusion probably occurs with hydrogen on tungsten and nickel and with oxygen on electropositive metals: copper, magnesium, etc.

If now we cover a plane metallic surface with $\sigma = \theta\sigma_1$ hydrogen atoms per cm.^{2}, θ being the fraction of the total number σ_1 of sites per cm.^{2} available to the adsorbate, we will form at the surface a double layer having its origin in the effective dipoles M_0. It will be first assumed that the dipoles M_0 do not interact with each other. Then we have $M_0 = ed$ (Fig. 1) where e is the electronic charge and d is the effective length of the dipole. The dipole layer affects both the work function φ_0 of the bare metal and the heat of adsorption q_0 on a bare surface. According to classical electrostatics, an electron moving from a point B inside the metal to a point A outside, will experience a constant force $F = 4\pi\sigma e^2$ at any point inside the double layer. The total

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(1) H. S. Taylor, *Proc. Roy. Soc. (London)*, **A108**, 105 (1925).

(2) H. S. Taylor, THIS JOURNAL, **53**, 578 (1931).

(3) N. F. Mott, *Proc. Camb. Phil. Soc.*, **32**, 281 (1936).

(4) I. Isenberg, *Phys. Rev.*, **79**, 737 (1950).

(5) B. Svensson, *Ann. Physik*, **18**, 229 (1933).

(6) A. Coehn and W. Specht, *Z. Physik*, **62**, 1 (1930).

(7) W. Himmler, *Z. physik. Chem.*, **195**, 244 (1950).

(8) D. A. Dowden, *J. Chem. Soc.*, 242 (1950).

work done due to the double layer will be $Fd = 4\pi e^2 d\sigma = 4\pi e M_0\sigma = 4\pi\sigma_1 M_0 e\theta$ and the work function will be modified by a corresponding amount: it is increased if the double layer is negative outwards and decreased in the opposite case: $\varphi = \varphi_0 \pm 4e\pi\sigma_1 M_0\theta$. This result has been extensively used for instance by de Boer[9] for the case of adsorption of metallic atoms. We can also write for the absolute value $\Delta\varphi$ of the change in work function corresponding to a coverage θ

$$\Delta\varphi = 4e\pi\sigma_1 M_0\theta \qquad (1)$$

The heat of adsorption of hydrogen should always decrease as a result of the presence of the double layer: $q = q_0 - \Delta q$ where $q_0 = q_b$ is the heat of binding corresponding to the formation of the covalent metallic bonds and Δq is a positive energy due to the effect of the double layer. If the latter is negative outwards, Δq corresponds to the work done in moving an electron from a point B inside the metal to a point C lying midway between the ends of the effective dipole (Fig. 1). This is a first approximation justified by the fact that in a covalent bond, the binding electrons spend most of their time in the region between the bound atoms. If the double layer is positive outwards, Δq is the work done in moving an electron from a point A outside the metal to a point C situated as before. In both cases, Δq is positive and equal to $F(d/2) = 2e\pi\sigma M_0 = 2e\pi\sigma_1 M_0\theta$. Thus the adsorption heat falls linearly with coverage and one has

$$\Delta q = 2e\pi\sigma_1 M_0\theta = 1/2\Delta\varphi \qquad (2)$$

The validity of equation (2) rests on two assumptions. First, there is no interaction between the dipoles M_0. Second the heat of binding q_b does not change with coverage, in other words, the change in heat is attributed solely to a change due to the effect of the double layer. The latter assumption is justified by the fact that the heat of solution of hydrogen in the interior of metals does not fall with increasing concentrations of dissolved hydrogen. For instance, in a recent investigation of the hydrogen–titanium system, McQuillan[10] has found that the heat of solution of hydrogen in titanium α was strictly constant whereas in titanium β the heat is constant below 10 atomic % of dissolved hydrogen and *increases* slowly for the further amounts of dissolved hydrogen. Thus, in titanium β, the heat per mole of hydrogen is 27.83 kcal. below 10 atomic % and reaches only 28.3 kcal. at 30 atomic %. The increase in heat of solution is probably due to an expansion of the lattice when increasing quantities of hydrogen are dissolved into it. The assumed constancy of q_b for the case of *surface* solution seems thus justified.

The other assumption introduced in the derivation of (2) is the neglect of interaction between the surface dipoles. The correctness of this approximation depends on the magnitude of M_0 and on the polarizability α of the adsorption complex. Owing to mutual depolarization of a plane array of dipoles, we have, in general, as shown by Miller[11]

$$M_\theta = M_0/[1 + (9\alpha\theta/a^3_1)]$$

where a_1 is the distance between dipoles for $\theta = 1$. Equation (1) now becomes

$$\Delta\varphi = 4e\pi\sigma_1 M_0\theta/(1 + k\theta) \qquad (3)$$

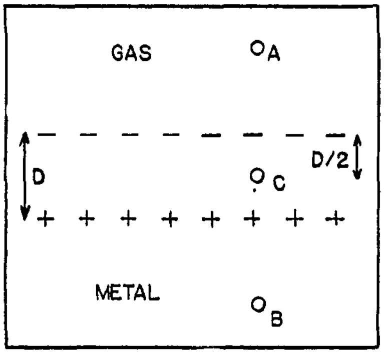

Fig. 1.

where $k = (9\alpha/a^3_1)$. For the adsorption of cesium on tungsten, the decrease in the work function as measured by the change in contact potential by Taylor and Langmuir[12] is well represented for $\theta < 0.4$ by equation (3) where $M_0 =$ 6.8 D as given by deBoer,[3] $\sigma_1 = 3.56 \times 10^{14}$ cm.$^{-2}$ and $k = 1.2$. This can be seen in the following table.

ADSORPTION OF CESIUM ON TUNGSTEN: $\Delta\varphi$ IN VOLTS

θ	$\Delta\varphi$ calcd.	$\Delta\varphi$ obsd.
0.167	1.28	1.31
.211	1.54	1.56
.231	1.66	1.66
.238	1.69	1.70
.263	1.82	1.82
.264	1.83	1.85
.298	2.00	1.99
.327	2.14	2.14
.333	2.17	2.17
.345	2.22	2.22
.349	2.25	2.24
.392	2.44	2.41

The empirical value $k = 1.2$ used in this calculation would correspond to $\alpha = 28.10^{-24}$ cm.^{3} for $a_1 = 6.3.10^{-8}$ cm. This value of α is intermediate between the values of α for the cesium ion and for the cesium atom, as might be expected. Taylor and Langmuir[12] have also measured the heat of evaporation of cesium atoms from a tungsten surface. The variation with coverage of the adsorption heat q of cesium on tungsten is determined however by three distinct factors: (1) the effect of the double layer, (2) the electrostatic repulsion between adsorbed atoms, (3) the attraction between cesium atoms to form clusters. It is because of this third factor that we are considering here only non-metallic atoms on metal surfaces. With metallic adatoms, the tendency to form metallic bonds between adatoms may become as great as the tendency to make metallic bonds between adatoms and metallic adsorbent. This is illustrated by the recent work of Becker[13] who studied adsorption of barium on tungsten by means of the field electron microscope. Becker suggests that barium forms two phases on the tungsten surface, a condensed phase (clusters) and a two-dimensional gas phase of individual adatoms. Thus, equation (2) may only be used for very low values of θ where both repulsion and attraction between adatoms may be neglected. Taylor and Langmuir found that $q = 67.4$ kcal. at $\theta = 0.002$ and $q = 62$ kcal. at $\theta = 0.05$. In this range of θ, φ decreases linearly with θ. Between these limits, $\Delta\varphi = 4e\pi\sigma_1 M_0$ $0.048 = 0.44$ e.v. $= 10$ kcal. if we take as before $M_0 = 6.8$ D and $\sigma_1 = 3.56.10^{14}$ cm.$^{-2}$. The observed value of Δq is 5.4 kcal. There is thus good agreement between this value and the calculated value $^1/_2\,\Delta\varphi = 5$ kcal. It is of interest to recall that Taylor and Langmuir ascribed the fall in q for $\theta < 0.05$ to "active spots" on the tungsten surface. Actually, this assumption is not necessary as first suggested by deBoer[9] and as shown here quantitatively. Thus, for adsorption of metal atoms, equation (2) has the character of a limiting law valid for small values of θ.

The fall in heats of adsorption of cesium on tungsten for $\theta > 0.05$ has been interpreted by Langmuir[14] in terms of interacting dipoles. A discussion of Langmuir's treatment lies beyond our scope since

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[9] J. H. deBoer, "Electron Emission and Adsorption Phenomena," Cambridge, 1935.

[10] A. D. McQuillan, *Proc. Roy. Soc. (London)*, **A204**, 309 (1950).

[11] A. R. Miller, *Proc. Camb. Phil. Soc.*, **42**, 292 (1946).

[12] J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44**, 432 (1933).

[13] J. A. Becker, *Bell System Tech. J.*, **30**, 907 (1951).

[14] I. Langmuir, THIS JOURNAL, **54**, 2798 (1932).

we restrict ourselves to cases where interaction plays a secondary role, at higher values of θ. Indeed in the case of hydrogen because of the very small value of α, there is no need to use equation (3), and equation (2) remains valid up to high values of θ. Thus, by measuring the contact potential of a tungsten wire covered with various amounts of hydrogen atoms, Bosworth[15] has found that φ increased linearly with θ. The highest value of θ reached by Bosworth is uncertain but according to a discussion of Rideal and Trapnell,[16] it must lie around $\theta = 0.7$, and not around $\theta = 1$ as believed earlier. Thus, equation (1) is valid and $\Delta\varphi = 1.04$ e.v. for the highest value of θ reached by Bosworth. On the other hand, Roberts[17] has measured calorimetrically the adsorption heat of hydrogen on a tungsten wire similar to that used by Bosworth and in similar conditions. Thus the maximum coverage in Roberts' experiment must be approximately the same as in the case of Bosworth. Roberts found a *linear* decrease of the adsorption heat from 45 kcal./mole of hydrogen for $\theta = 0$ to 18 kcal./mole at the highest value of θ. Thus $\Delta q = (45 - 18)/2$ kcal./atom. According to equation (2), one should have $\Delta q = {}^1/_2\,\Delta\varphi$. Since $\Delta q = 13.5$ kcal. and ${}^1/_2\,\Delta\varphi = {}^1/_2$, 1.04 e.v. = 12 kcal., the agreement is quite satisfactory. It is to be emphasized that *this linear fall in heat is not due to interactions between dipoles*, otherwise equation (1) would not be obeyed. Rideal and Trapnell[16] have calculated that dipole–dipole interactions for hydrogen on tungsten would account for only 2 kcal. of the total Δq. It is certain however that direct interaction between adsorbed hydrogen atoms must come into play for values of θ approaching unity.

It may be argued that the surface of the tungsten wire used by Bosworth and Roberts is not the ideal plane surface assumed at the start but presents various crystallographic planes, corners, edges, dislocations and grain boundaries. The fall in heat Δq might then be explained by assigning a continuous range of adsorption energies to the various sites thus defined. The linear increase in work function $\Delta\varphi$ is much more difficult to explain on such a basis. It is convenient to call "*a priori* heterogeneity" such an explanation of decrease in adsorption heats with coverage. This explanation invoking "*a priori*" active centers existing on the surface before adsorption sets in is to be contrasted with the picture presented above to which we have given before[18] the name of induced heterogeneity. The latter term seems confusing however and the effect will be called "induction." It is quite essential to remark that induction as here presented must be sharply distinguished from any kind of interaction parallel to the surface and determined by the distance between adatoms. Halsey and Taylor[19] have demonstrated that no interaction theory on a uniform surface can explain a differential heat of adsorption with increased coverage which has an initial slope $dq/d\theta$ greater than 0.25 q_0. Thus, even with some unknown force of interaction "transmitted through the solid"[16] and of an order of magnitude sufficient to explain the over-all decrease in adsorption heat, the objection of Halsey and Taylor would still hold. No such restriction is placed upon the mechanism of induction.

We have limited ourselves so far to the case of hydrogen on a metal surface. Quite generally however, chemisorption at a metal surface brings about collectivization of the bonding electrons between adsorbate and metal with formation of covalent resonating bonds and of a double layer. In general, if n is the number of valence electrons of the adatom taking part in the bonding

$$\Delta q = 2ne\pi\sigma_1 M_0\theta = n/2\Delta\varphi \qquad (2a)$$

Numerous cases are reported where the adsorption of hydrogen, nitrogen and oxygen change the work function of the underlying metal. Only three other cases are known to the writer where both heat and work function data are available simultaneously with their dependence on coverage, so that a check of formula (2) can be made.

Mignolet[20] has found that the work function of a nickel evaporated film was increased by 0.345 e.v. by adsorption of hydrogen atoms. Thus $\Delta\varphi = 7.95$ kcal. Beeck on the other hand measured calorimetrically the differential adsorption heat of hydrogen on a nickel film.[10] The latter falls almost linearly from 30 kcal./mole for $\theta = 0$ to 20 kcal./mole for the maximum coverage reached. If this value, as seems reasonable, is also that attained in Mignolet's experiment, then we must have: $\Delta q = {}^1/_2\,(30 - 20)$ kcal./atom $= {}^1/_2\,\Delta\varphi = 4$ kcal. The agreement is satisfactory.

Bosworth[21] has measured $\Delta\varphi$ for a tungsten wire covered with nitrogen at 90°K. He found a linear increase in the range measured. Equation (1) is thus obeyed and here, also, no direct interaction between surface dipoles is noticeable. For the highest value of θ, he gets: $\Delta\varphi = 1.38$ e.v. = 31.8 kcal. Whereas no calorimetric data are available in this case, Beeck[22] states that chemisorption of nitrogen on a tungsten film evolves 95 kcal./mole at 300°K. whereas the adsorption heat at lower temperatures is smaller. The inference is that at 300°K., nitrogen is chemisorbed as atoms whereas it is chemisorbed without dissociation at lower temperatures. This is confirmed by the adsorption heats which Bosworth and Rideal[23] calculated from rates of evaporation of nitrogen adsorbed at 90°K. on a tungsten filament; the rates were determined by following the change of contact potential with time. Bosworth[21] has plotted those values of the heat as a function of coverage. The heat decreases approximately linearly from about 30 kcal./mole for $\theta = 0$ to about 15 kcal./mole for the highest value of θ reached in the experiment. Comparison with Beeck's data shows that nitrogen is not dissociated on tungsten at 90°K., so that one must have: $\Delta q = (30 - 15)$ kcal./mole $= {}^1/_2\,\Delta\varphi = 15.9$ kcal. Here also, the agreement is satisfactory.

Oxygen chemisorption on tungsten illustrates two points of interest. First, since oxygen is divalent, $n = 2$ in formula 2a; in the former representations of the chemisorption complex, this would be expressed by either W═O or $W^{++}O^{--}$. Actually, the chemisorption bonds are intermediate in character between the pure covalent and the ionic types. Second, in view of the larger polarizability of oxygen, lateral interaction between surface dipoles should become observable at lower values of θ than in the case of hydrogen. Bosworth and Rideal[23] and later Bosworth[24] have measured the work

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[15] R. C. L. Bosworth, *Proc. Camb. Phil. Soc.*, **33**, 394 (1937).

[16] E. K. Rideal and B. M. W. Trapnell, *J. chim. phys.*, **47**, 126 (1950).

[17] J. K. Roberts, *Proc. Roy. Soc.* (*London*), **A152**, 445 (1935).

[18] M. Boudart, THIS JOURNAL, **74**, 1531 (1952).

[19] G. Halsey and H. S. Taylor, *J. Chem. Phys.*, **15**, 624 (1947).

[20] J. C. P. Mignolet, Faraday Soc. Discussion on Heterogeneous Catalysis, p. 105 (1950).

[21] R. C. L. Bosworth, *Trans. Roy. Soc.*, *N.S.W.*, **79**, 166 (1946).

[22] O. Beeck, "Advances in Catalysis, II," Academic Press, Inc., New York, N. Y., 1950.

[23] R. C. L. Bosworth and E. K. Rideal, *Physica*, **4**, 925 (1937).

[24] R. C. L. Bosworth, *Trans. Roy. Soc.*, *N.S.W*., **79**, 53 (1946).

function and the adsorption heat of oxygen atoms on a tungsten wire by means of a contact potential technique. They found that the heat decreases approximately linearly up to a value of $\theta = 0.5$ from about 150 kcal./mole to about 90 kcal./mole. Beyond $\theta = 0.5$, the heat curve decreases less rapidly, a value of 60 kcal./mole being reached at $\theta = 1$. The work function on the other hand increases linearly with θ up to $\theta = 0.5$, then less rapidly for higher values of θ: between $\theta = 0$ and $\theta = 0.5$, $\Delta\varphi = 1.05$ e.v. $= 24$ kcal. According to (2a), this is to be compared to $\Delta q = 1/2(150 - 90) = 30$ kcal./atom. Beyond $\theta = 0.5$, lateral dipole interactions set in and (2a) is not applicable.

The five cases analyzed above are summarized in the following table.

Δq(kcal.)	H_2 on W	H_2 on Ni	O_2 on W	N_2 on W	Cs on W
calcd.	12	4	24	15.9	5
obsd.	13.5	5	30	15	5.4

Thus, the semi-classical mechanism depicted here is able to explain the *order of magnitude* of the fall in adsorption heats on clean metal surfaces. It does not seem that a more refined treatment would bring in any essentially new feature.

Induction on a Metal Surface.—It has been said earlier that the fall in adsorption heat of hydrogen on a tungsten wire might possibly be explained by means of *a priori* heterogeneity although such an explanation does not seem probable. Beeck however has provided a clear-cut case[22] where *a priori* heterogeneity is excluded. Beeck has found that nitrogen chemisorption on an iron film is activated at room temperature and stops after only one-fifth of the total surface available to hydrogen at the same temperature has been occupied. It will be assumed, for the sake of simplicity, that $\theta = 1.0$ when hydrogen covers the iron film. Thus, on a bare iron surface, nitrogen chemisorption stops at $\theta = 0.2$. However, if some fraction θ_H of the surface is previously covered with hydrogen, nitrogen may still be subsequently adsorbed and it will cover a fraction θ_N of the surface equal to one-fifth of the remaining bare surface. Beeck found a linear relationship

$$\theta_N = 0.2\,(1 - \theta_H) \qquad (5)$$

The adsorption heats for both gases chemisorbed separately have been measured calorimetrically by Beeck: for both hydrogen and nitrogen, $q \cong 40$ kcal./mole at $\theta = 0$ whereas $q \cong 15$ kcal. for $\theta_N = 0.2$ and $\theta_H = 1.0$. As noted by Beeck, *a priori* heterogeneity is unable to account for these observations. Indeed, no nitrogen chemisorption should take place on a surface covered with hydrogen for all values of θ_H larger than 0.2, since then all *a priori* active centers available to nitrogen should already be covered with hydrogen. Equation (5) may not be interpreted either by assuming that nitrogen is adsorbed "on top" of hydrogen with possible formation of NH complexes since $\theta_N = 0$ when $\theta_H = 1$. Beeck, while recognizing the inadequacy of *a priori* heterogeneity in this case, put forward no interpretation of his experimental findings. The data are susceptible of a novel explanation in terms of induction. Since nitrogen is more electronegative than hydrogen, it should raise the work function φ of iron more rapidly than the latter. It will be assumed that hydrogen actually raises the work function of a clean iron surface, as is the case for tungsten and nickel. (For a contrary opinion see ref. 25.) Since an increase in φ is accompanied by a decrease in q and thus, by a rise in activation energy for adsorption, the activated adsorption of nitrogen will become immeasurably slow after only a fraction of the surface has been covered. In Fig. 2, the region above CD is "forbidden" to nitrogen at room temperature. On a clean surface, adsorption of hydrogen and nitrogen proceeds along AD and AB, respectively. If a fraction $\theta_H = CC_1$ of the surface is previously covered with hydrogen, a fraction of C_1B_1 of the surface will be subsequently covered with nitrogen, the adsorption of which proceeds along A_1B_1 parallel to AB. Since $CB:C_1B_1 = AC:A_1C_1 = CD:C_1D$, we get $C_1B_1:C_1D = CB:CD$. But $CB:CD = 0.2$. Thus: $C_1B_1 = 0.2 \times C_1D$ or $C_1B_1 = 0.2\,(1 - CC_1)$, which is the relation found by Beeck.

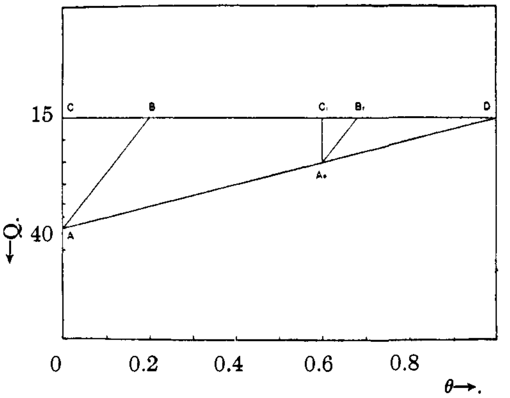

Fig. 2.

It must be kept in mind that Beeck's experiment was carried out with an iron evaporated film. Such films must be characterized by an *a priori* heterogeneity of the highest degree: dislocations, distorted crystallites of various shapes and sizes limited by all conceivable crystallographic planes, atoms in abnormal positions, etc. The fact that *a priori* heterogeneity fails to explain the observed mutual interference of adsorbed hydrogen and nitrogen becomes then even more significant. As a matter of fact, most of the calorimetric differential heat curves on evaporated films present a more or less marked departure from linearity, although they are well approximated by a straight line in the middle adsorption range. Quite generally, on a clean metal surface presenting *a priori* heterogeneity, the complete heat curve from $\theta = 0$ to $\theta = 1$ is the result of the superposition of three distinct phenomena: (1) *a priori* heterogeneity, (2) induction, (3) lateral interaction between adsorbed species. Especially in view of the fact that *a priori* heterogeneity is a structure-sensitive property of the adsorbent depending on its previous history, it does not seem possible to give to the heat curve a meaningful functional form over a complete range of coverage. From the examples treated above, it is seen however that induction is of predominating importance in explaining the magnitude of the heat fall up to the value of θ where lateral interaction becomes important.

Induction on a metal surface takes place because of the covalent metallic nature of the adsorption bonds. Consequently, it ought to be entirely absent in the case of van der Waals adsorption. This is actually the case: Rhodin,[24] studying the van

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(25) J. H. deBoer, *Chem. Weekblad*, **47**, 416 (1951).

(26) T. N. Rhodin, THIS JOURNAL, **72**, 569 (1950).

der Waals adsorption of nitrogen on single crystal copper surfaces found that the adsorption heat stays constant during the beginning of the formation of a monolayer until attraction forces between nitrogen molecules bring about an *increase* in the adsorption heat. This result has to be compared with the effect recently discovered by Mignolet.[20] He found that van der Waals adsorption could be responsible for sizeable changes in the work function of nickel: for xenon, the decrease in work function $\Delta\varphi$ reaches the very high value of 0.85 e. v. In the case of van der Waals adsorption, however, a change in φ does not entail a change in q as is true for chemisorption.

Induction on Contaminated Metal Surfaces.—In order to be adequate, a theory of chemisorption must explain, at least qualitatively, the salient facts relative to poisons and promoters. This will be done briefly in this paragraph, the contents of which are frankly speculative. It is felt necessary, however, to account for the types of phenomena which were formerly interpreted in terms of *a priori* heterogeneity.

Let us consider once more the adsorption of nitrogen on an iron surface. We have been led to the conclusion that the work function of iron is increased by nitrogen adsorbed along AN (Fig. 3) to such an extent that at room temperature, the activated adsorption of nitrogen stops after point N has been reached: the region above CD is forbidden to nitrogen at 300°K. Suppose however that the iron surface is not clean but is contaminated with oxygen: since the latter is more electronegative than nitrogen, the work function of iron ought to rise along AB, point B lying at the boundary of the zone forbidden to nitrogen and at a value of θ which may be taken as, say, $\theta = 0.1$ to 0.15. This means that, if a fraction of the iron surface less than 0.15 is covered with oxygen, no nitrogen chemisorption will take place on that surface at room temperature. The poisoning effect of traces of oxygen capable of covering only 10 to 15% of an available iron surface has been extensively studied in connection with ammonia synthesis[27,28] which involves nitrogen chemisorption as one of its steps. It may be surmised that an electropositive atom such as aluminum or potassium would have exactly the opposite effect now decreasing φ along, say, AF: nitrogen chemisorption would proceed along FG at room temperature; potassium would then be a promoter for nitrogen chemisorption. If on the other hand, a small quantity ($\theta = 0.15$) of potassium is adsorbed on an iron surface already poisoned with a small quantity of oxygen, nitrogen chemisorption may proceed along KS at 300°K. Thus we are led logically to consider complex [Fe–O–Al–K] surfaces. This, according to the evidence accumulated by Emmett and his collaborators,[29] corresponds precisely to the description of doubly promoted synthetic ammonia catalysts. The fact that alumina and potash counterbalance the poisoning effect of oxygen on an iron surface thus receives here a simple explanation. Although the properties of [Fe–O–K] surfaces have not been studied from the viewpoint of the present discussion, the behavior of [W–O–Cs] and similar surfaces is of course well known.[30] For a [W–O–Cs] surface, for instance, it will be recalled that cesium is bound more tightly on a tungsten surface contaminated with oxygen than on clean tungsten. Such a result can be understood at once by a diagram similar to that of Fig. 3 and by the formula found above relating $\Delta\varphi$ and Δq.

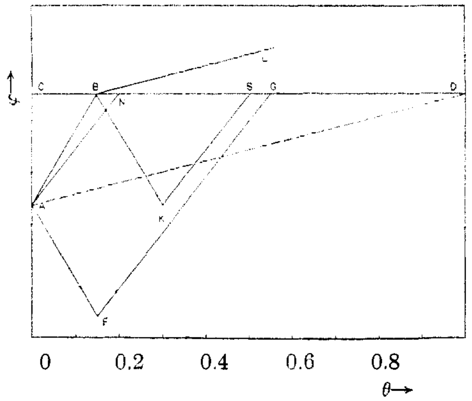

Fig. 3.

The vast majority of chemisorption data on metals has been obtained with contaminated surfaces. On such surfaces, even the chemisorption of hydrogen which proceeds with practically no activation energy at very low temperatures on several metals with unfilled *d*-bands may become a slow activated process. A good sign of contamination presumably by oxygen is the considerably lower value of q_0, the adsorption heat of hydrogen on a "bare" metal surface. Thus, on a "pure" iron powder reduced during six months at 500° in pure hydrogen, Kwan[31] has found an initial isosteric adsorption heat of hydrogen equal to 17.5 kcal./mole. This value is much smaller than the value of about 40 kcal./mole measured calorimetrically by Beeck on an iron film. Here again, if only a fraction of the iron surface equal to 0.15 was contaminated with oxygen, hydrogen chemisorption would follow along BL (Fig. 3) and not along AD as it would on a clean surface. On the preceding diagram (Fig. 2) it can be seen that the initial heat would then be about 15 kcal./mole in agreement with Kwan's result. It is equally possible that in view of the findings of Emmett and Kummer[32] that Kwan's iron surface was contaminated with nitrogen present in the hydrogen used for the reduction. This would not change the present discussion.

Contamination by oxygen has a poisoning effect when it forms a double layer negative outwards and when the subsequently adsorbed gas has a similarly directed dipole. On the contrary, if oxygen decreases the work function of a given metal, oxygen is a promoter for chemisorption of a gas forming a double layer negative outwards. This might well be the case for hydrogen chemisorption on copper. Whereas copper films do not take up hydrogen at room temperature, adsorption and sorption of hydrogen by copper powders obtained by reduction of a copper salt have been measured repeatedly even at 0°.[33] Fianda and Lange[34] have recently shown that oxygen *lowers* the work function of copper and other electropositive metals. Thus, a [Cu–O] surface should bind hydrogen more tightly than clean copper if, as is reasonable to assume, hydrogen forms a dipole negative outwards on copper. Consequently, hydrogen chemisorption should be more rapid (lower activation energy) on a copper surface "promoted" by small quantities of oxygen.

Finally, it appears appropriate to discuss briefly the data which Frankenburg[35] obtained with tungsten powders. The surface of these powders was *rigorously clean* as shown by the same value of q_0 as that measured on films and wires. However, Frankenburg's outgassing procedure was almost certainly unable to drive off an unknown amount of hydrogen sorbed in the interior of the metal particles. This "sorption contamination," the reality of which can easily be demonstrated with palladium[36] by its effect on the surface *p*-hydrogen conversion explains why the isosteric heats of Frankenburg, below 529°, show a linear drop from about 45 kcal. at $\theta = 0$ to about 20 kcal. at $\theta = 0.1$ and a much slower decrease down to 12 kcal. at $\theta = 0.3$, so that the heat curve is apparently fitted by an exponential function. Indeed, this linear drop followed by a slower decrease of the adsorption heat would be accounted for in our scheme by a value of the effective moment M_0, about five times larger

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than on the tungsten surface of Roberts and Bosworth. That this may be a consequence of "sorption contamination" is shown by the contact potential data of Mignolet.[20] On a clean nickel film, the contact potential difference after hydrogen chemisorption at 20° is −0.345 v., as befits an adsorption layer negative outward. At 20°, some of this hydrogen[22] is absorbed, so that further adsorption occurs by cooling down, on the surface sites left vacant by the migration of hydrogen into the interior. Mignolet found that by cooling at −196°, a new quantity of hydrogen is adsorbed corresponding to about 0.03% of the quantity presorbed at 20°: at the same time, the contact potential difference becomes more positive by about 0.1 v. This shows that hydrogen adsorbed on "sorption contaminated" sites has an effective dipole M_0 of a sign opposite to that of hydrogen adsorbed on pure nickel and of a considerably larger value (about eightfold). This can be understood if we recall our definition of M_0: if hydrogen is sorbed below the surface, adsorbed hydrogen will not be able to penetrate so deeply in the surface layer: since the individual dipole moments between hydrogen and metal atoms A are of the type A^-–H^+, the resulting dipole M_0 will now become positive outward. That its value is considerably larger than that on the pure metal is shown by the data of Mignolet for nickel. Since nickel and tungsten show very similar surface potential properties when covered with hydrogen, we surmise that essentially the same type of "sorption contamination" takes place with tungsten.[37] It is to be remarked that the value of q_0 is the same on the clean surface of a pure metal and of a sorption contaminated metal, since q_0 is determined by the number of bonds between the adatom and the neighboring metal atoms. This number is not changed by a small displacement of the adatom vertically to the surface, while M_0 is very sensitive to such a displacement, being the resultant of a number of dipoles. Hydrogen absorption which occurs in tungsten films, is also evidenced in the case of Frankenburg's powders by a strong decrease of q_0 above 529°. At these high temperatures, absorption becomes more pronounced and q_0 must decrease as a result of the endothermic heat of absorption. The present interpretation of Frankenburg's data seems the only one which explains: (1) the same value of q_0 as that on a wire or film, whereas the assumption of a "dirty" surface necessitates a different value of q_0; (2) the concavity of the heat curve which occurs when dipole–dipole interactions become important, whereas the explanation advanced by Beeck[22] does not lead to such a heat curve and is based on the *ad hoc* assumption that 75% of the powder surface is covered with silica.

Induction in Catalysis.—Conducting and semiconducting surfaces[18] present induction in chemisorption. The fact that these surfaces may nevertheless behave in catalysis as if they were homogeneous, is a well-known paradox which can easily be resolved by admitting that only a small fraction of the surface is active at any time during the catalytic reaction. That part of the surface defines the "optimum" or "active" centers characterized by a maximum rate for all steps or the slowest step of the catalytic process.[38] The results obtained by assuming a continuous distribution of energy sites at the surface[38,39] are valid whatever may be the nature of the heterogeneity defined in a purely phenomenological way. The origin of heterogeneity and thus the nature of the active centers becomes of interest in connection with the ultimate explanation of catalytic action and of its modification by promoters and poisons. For the *p*-hydrogen conversion on tungsten film, Rideal and Trapnell[16] have made it abundantly clear that, at low temperatures, only a small fraction of the surface is active at any time, namely, the fraction corresponding to high values of θ for which the heat of chemisorption becomes very small. Thus, in this case, induction which is responsible for the major part of the lowering of the adsorption heat is a necessary condition for catalysis. Quite generally, catalysis at a clean metal surface does not seem possible at all without induction, except perhaps at very high temperatures, since the heat of chemisorption on clean and bare metal surfaces is so high that it makes chemisorption irreversible. One might say that clean metal surfaces never behave as catalysts. They will be first covered with reactants, products, promoters or poisons which radically modify the adsorbing properties of the original bare surface. Induction thus appears as a mechanism by which conducting surfaces acquire the optimum sites required for a particular reaction carried out in given conditions of pressure or temperature. It is truly a characteristic of contact catalysis as opposed to homogeneous (*e.g.*, acid–base) molecular catalysis. Indeed, insulators, *e.g.*, silica–alumina, which do not possess the property of induction are used for reactions operating through a proton switch or carbonium ion mechanism; such reactions may however be also performed homogeneously. On the contrary, catalysis by conducting surfaces is a coöperative phenomenon involving the whole surface even if only a small fraction of it is active at any time. Of course, induction is by no means a sufficient condition for catalysis. The change in adsorption heat Δq has been considered exclusively in the present work. An examination of the absolute values of adsorption heats and activation energies lies beyond our scope, although these values will decide in the last analysis whether a given surface will catalyze a particular reaction.

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(37) NOTE ADDED DURING PROOF.—More recent data of Mignolet (*J. Chem. Phys.*, **20**, 341 (1952)) give additional weight to this particular statement.

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